



ANALYSIS OF THE OXYGEN ISOTOPIC COMPOSITION OF WATER SAMPLES USING THE ISOPREP 18

PROCEDURE ID: YMP-LBNL-TIP/TT10.0

REV. 0, MOD. 0

EFFECTIVE: 09/30/98

1. PURPOSE

This Technical Implementing Procedure (TIP) describes a method to analyze the ^{18}O values of water samples using the Fisons Instruments Isoprep 18 unit (Isoprep) for the Yucca Mountain Site Characterization Project (YMP) at Lawrence Berkeley National Laboratory (LBNL).

2. SCOPE

This procedure shall be used by all LBNL personnel (or contractor personnel following LBNL procedures) involved in YMP activities whenever they are required to analyze the oxygen isotopic composition (^{18}O value) of water samples. Prior to conducting work described in section 3.0 of this procedure, personnel require training to this procedure.

If this procedure cannot be implemented as written, YMP-LBNL personnel shall notify the responsible Principal Investigator (PI) or designee. If it is determined that a portion of the work cannot be accomplished as described in this TIP, or would produce undesirable results, that portion of the work shall be stopped and not resumed until this procedure is modified per YMP-LBNL-QIP-5.2, *Preparing Quality & Technical Implementing Procedures*.

If the responsible PI or designee determines that a modification or a revision to the TIP would cause an unreasonable delay in proceeding with the task, then an expedited change to the procedure, including documentation of deviation from the approved procedure, can be made according to YMP-LBNL-QIP-5.2. Such changes are subject to review, usually after the task has proceeded, and thus work performed under TIPs with expedited changes is done at risk of future invalidation.

Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used. When this procedure becomes obsolete or superseded, it must be destroyed or marked "superseded" to ensure that this document is not used to perform work.

3. PROCEDURE

3.1 Principle

This procedure outlines an automated technique for analyzing the ^{18}O values of water samples using the Isoprep. CO_2 is isotopically

equilibrated with the water sample at a constant temperature. The ^{18}O value of the CO_2 gas is then analyzed using the VG Isotech Prism Series II Isotope Ratio Mass Spectrometer (Prism). The ^{18}O value of the water can then be calculated from the ^{18}O value of the CO_2 . Because the amount of oxygen in the water is much greater than the amount of oxygen in the CO_2 , no correction for exchange between the two is necessary.

3.2 Materials/Equipment Required

- 0-5 ml pipette with disposable tips
- Equilibrator flasks
- Large stainless steel dewar
- Liquid N_2 (LN)
- Methanol
- Cryocooler
- Fisons Instruments Isoprep 18 (Isoprep) and operating manual
- VG Isotech Prism Series II Isotope Ratio Mass Spectrometer (Prism) and operating manuals
- Water standards (NIST standards VSMOW, GISP and SLAP and internally calibrated water standards)

3.3 Sample Run Set-up

- 3.3.1 Records generated as a result of this TIP shall be entered into the appropriate YMP scientific notebook in accordance with YMP-LBNL-QIP-SIII.0, *Scientific Investigations*. Applicable elements of the laboratory notebooks are incorporated into the scientific notebook.
- 3.3.2 Pipette the water samples into the equilibrator flasks (minimum size equals 0.5 ml) using a separate pipettor tip for each sample. Load standards in ports AA, BA, AL, and BL (Attachment 2) and unknowns in the remaining 20 ports. Attach the samples to the inlet ports of the Isoprep by tightening Cajon fittings on the ports onto the neck of the equilibrator flasks (Attachment 1).
- 3.3.3 Evacuate the air in the sample flasks by opening all the inlet ports and waiting until the Pirani gauge reads <0.5 mbars (Attachment 2).

- 3.3.4 Close all ports and evacuate the air remaining in the sample banks. Open all ports, switch over the three way bank selection valves and open the CO₂ gas valve to fill the equilibrator flasks with CO₂. The pressure of CO₂ in the CO₂ reservoir should be between 200 and 400 millibars. Wait one minute.
- 3.3.5 Close the CO₂ gas valve, close all ports, and pump away the CO₂ remaining in the pipework.
- 3.3.6 Place the Plexiglas cover over the sample banks on the equilibrator, turn on the heater to regulate the temperature at 25°C and begin to shake the flasks. Equilibrate the samples for at least 6 hours before beginning the sample run.
- 3.3.7 Fill a large stainless steel dewar with methanol to ~2" from the top of the dewar. Chill the methanol with liquid N₂ until it begins to freeze on the sides of the dewar. Place the dewar on the water trap of the Isoprep. Insert the probe of the Cryocooler into the methanol and turn on the Cryocooler (in order for the temperature of the methanol to stabilize at -90°C, do this at least 30 minutes prior to beginning a sample run).
- 3.4 Analysis of the Oxygen Isotope Ratios of the Equilibrated CO₂ (for further information, refer to the Operating Manual for the mass spectrometer)**
- 3.4.1 The carbon (¹³C) and oxygen (¹⁸O) isotopic ratios of CO₂ are analyzed using the VG Isotech Prism Series II Isotope Ratio Mass Spectrometer (Prism) in Room 4425 of Building 70A at LBNL. This analytical procedure is automated using the **Dual Inlet** software. The software used to control sample analysis with the mass spectrometer is an integral part of the mass spectrometer and thus controlled by YMP-LBNL-QIP-12.0, *Control and Calibration of Measuring and Test Equipment*. In essence, the CO₂ gas is expanded into the sample bellows of the Prism and then bled into the ion source of the mass spectrometer through capillary tubing. In the ion source, the stream of CO₂ gas is bombarded with a beam of electrons which cause a fraction (~1%) of the CO₂ to become ionized to CO₂⁺. The CO₂ ions are then accelerated out of the ion source, through a series of electronic lenses which collimate the ions into a narrow beam. The ion beam is then passed through a strong magnetic field where it is bent. The amount that the CO₂ ions are deflected by the magnetic field is a function of the mass of the ions (e.g., ¹²C¹⁶O₂ = mass 44, ¹³C¹⁶O₂ = mass 45 and ¹²C¹⁸O¹⁶O = mass 46). As a result, the ion beam is separated into 3 beams. The relative intensities of these beams are then measured with Faraday cups positioned in the paths of the three ion beams. From

the ratios of the intensities of the 3 beams (mass 45/mass 44 and mass 46/mass 44), the ^{13}C and ^{18}O values of the CO_2 can be calculated.

During analysis of the samples, the isotopic ratios of the gas will be shifted slightly and the sensitivity of the machine will drift. To correct for these systematic errors, a standard gas with known isotopic ratios is analyzed at the same time as the sample (in 10-12 alternating blocks of 10-20 seconds each). The data for the sample is then corrected relative to the data for the standard. The procedure for calibrating the standard gas is discussed in detail in YMP-LBNL-TIP/TT11.0, *Calibration of a Mass Spectrometer for Isotopic Measurements of CO_2 and H_2* .

- 3.4.2 To analyze the isotopic ratios of the CO_2 that has been equilibrated with the water samples in the Isoprep, enter the sample run data into the computer (autorun set up file Iso18).
- 3.4.3 Check the tuning of the mass spectrometer by letting standard gas into the mass spectrometer and doing a peak center (Control C). If the sensitivity is low (for a beam 1 reading of $7\text{e-}9$ amps, the ion gauge reading should be less than or equal to $1\text{e-}7$) or the peak shape is bad (not symmetric or choppy), adjust the tuning of the mass spectrometer or find someone who is able to do that.
- 3.4.4 When the tuning is set, make sure there is adequate standard gas for the sample run (to obtain a beam 1 reading of $7\text{e-}9$ amps, the position of the standard bellows should be less than or equal to 2500), check that the toggle switch between the Isoprep and the inlet to the mass spectrometer is open and start the autorun.
- 3.4.5 When the run is finished, enter the run data in the Prism log book.
- 3.4.6 Compare the accepted values of the standards to the values measured. If they are offset, correct the unknowns by the average offset of the standards. If the offset of the standards is more than 1‰ from the accepted value or the range of values measured for the standards is more than 0.4%, reject the data and redo the analyses.

4. RECORDS

4.1 Lifetime

Records generated as a result of this TIP are entries in scientific notebooks or attachments to such notebooks.

4.2 Non-Permanent

None

4.3 Controlled Documents

Technical Implementing Procedure

4.4 Records Center Documents

Records associated with this procedure shall be submitted to Records Processing Center in accordance with AP-17.1Q, *Record Source Responsibility for Inclusionary Records*.

5. RESPONSIBILITIES

5.1 The **Project Manager** is responsible for final approval of the new, revised or modified TIP and for final approval of the rescission of the TIP.

5.2 The **EA Manager** is responsible for approving the new, revised or modified TIP, and for the rescission of the TIP.

5.3 The **OQA Representative** is responsible for reviewing and concurring with the TIP.

5.4 The **Principal Investigator (PI)** or designee is responsible for assuring full compliance with this procedure and for providing training thereof. The PI or designee is also responsible for overseeing and coordinating the preparation, review, distribution, revision, and rescission of the TIP.

5.5 **Staff Members** are responsible for following this procedure and turning over related documentation to the Records Coordinator for submittal to the Records Processing Center in accordance with AP-17.1Q. Related data shall be turned over to the Technical Data Coordinator in accordance with YMP-LBNL-QIP-SIII.3, who will be responsible for submitting key data to the Yucca Mountain Project Office for entry into the YMP Technical Data Base (TDB).

5.6 **Document Control Staff** are responsible for providing the controlled distribution of the TIP and modifications thereof.

6. ACRONYMS AND DEFINITIONS

6.1 Acronyms

| | |
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| CIG | Center for Isotope Geochemistry |
| EA | Engineering Assurance |
| LBNL | Lawrence Berkeley National Laboratory |
| LN | Liquid nitrogen |
| OQA | Office of Quality Assurance |
| PI | Principal Investigator |
| TDB | Technical Data Base |
| TIP | Technical Implementing Procedure |
| YMP | Yucca Mountain Site Characterization Project |

6.2 Definitions

Isoprep: Fisons Instruments Isoprep 18 in Room 4425 of building 70A at LBNL.

Prism: VG Isotech Prism Series II Isotope Ratio Mass Spectrometer in Room 4425 of building 70A at LBNL.

Staff Member: Any scientist, engineer, research or technical associate, technician, or student research assistant performing quality-affecting work for YMP-LBNL.

Technical Implementing Procedure: Each TIP describes YMP-LBNL technical tasks that (1) are repetitive, (2) are standardized, and (3) can return different results if deviation from the sequence of steps occur.

7. REFERENCES

AP-17.1Q, *Record Source Responsibility for Inclusionary Records.*

YMP-LBNL-QIP-5.2, *Preparing Quality & Technical Implementing Procedure*

YMP-LBNL-QIP-12.0, *Control and Calibration of Measuring and Test Equipment*

YMP-LBNL-QIP-SIII.0, *Scientific Investigations*

YMP-LBNL-QIP-SIII.3, *Submitting Key Data to the Yucca Mountain Project Office*

YMP-LBNL-TIP/TT 11.0, *Calibration of a Mass Spectrometer for Isotopic Measurements of CO₂ and H₂*

8. ATTACHMENTS

Attachment 1 - Sketch of an equilibrator flask and a Cajon connector for attaching the flask to the sample manifold of the Isoprep.

Attachment 2 - Schematic diagram of the valve configuration of the Isoprep (only sample bank A is shown on this diagram; there is also a sample bank B).

9. REVISION HISTORY

09/30/98 – Revision 0, Modification 0:

This is the initial issue of this procedure. It is derived from a scientific notebook procedure “Analysis of the ^{18}O Values of Water Samples Using the ISOPREP 18” in Notebooks YMP-LBNL-YWT-MC-1 and YMP-LBNL-JSW-MC-1.

10. APPROVAL

Preparer: Mark Conrad

Date

Technical Reviewer: Nick Spycher

Date

Technical Reviewer: Eric Sonnenthal

Date

EA Reviewer: Nancy Aden-Gleason

Date

OQA Concurrence: Stephen Harris

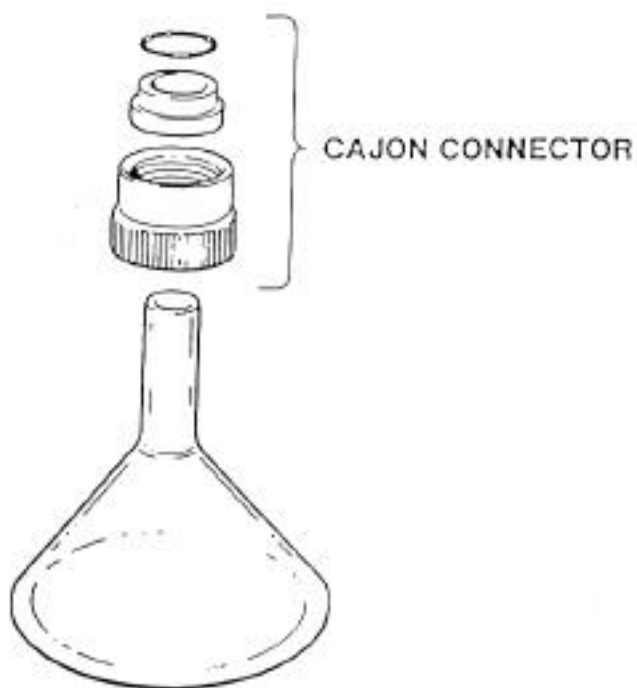
Date

Principal Investigator: Yvonne Tsang

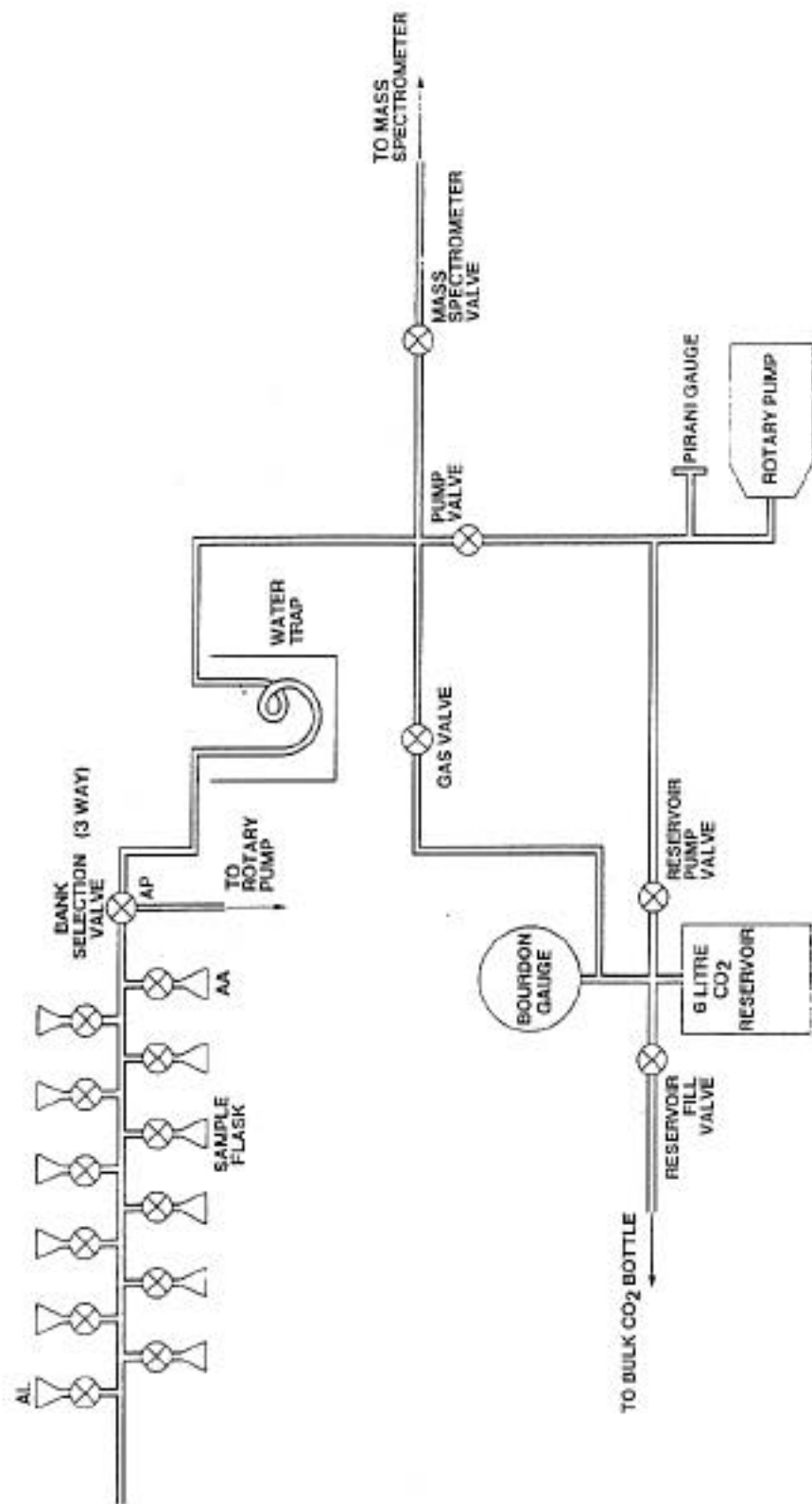
Date

Project Manager: Gudmundur Bodvarsson

Date



Attachment 1 - Sketch of an equilibrator flask and a Cajon connector for attaching the flask to the sample manifold of the Isoprep (from ISOPREP 18 User Manual).



Attachment 2 - Schematic diagram of the valve configuration of the Isoprep (only sample bank A is shown on this diagram; there is also a sample bank B). Diagram reproduced from ISOPREP 18 User Manual.